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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

02405651.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

DEN HAAG, DEN
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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

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Organic solvent-based gravure printing inks

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Organic Solvent-Based Gravure Printing Inks

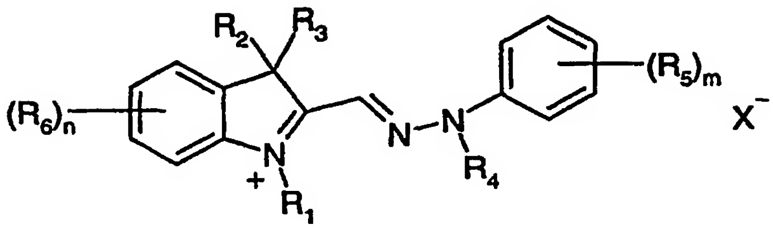
The present invention relates to organo-soluble compositions containing basic yellow dyes of the indole class as sole colourant or as toner (toning agent) for predominatly pigment based inks which are useful as gravure printing inks in e.g. publication gravure or packaging gravure printing processes. The yellow dyes are prepared from their carbinol base precursors by reacting them with organic acidic components, before or during (in-situ) the process for preparing the prining inks.

The use of certain colour bases (carbinols) for the preparation of organic solvent-based gravure inks is already disclosed e.g. in FATIPEC CONGRESS 1976, 13, 554 where dyes and associated carbinols of the triarylmethane, diarylmethane and xanthene families are combined with coloured pigment compositions containing a so-called printing resin. The use of indole dyes and their cabinols is not mentioned, and further, the effects, e.g. colour strength, can be visibly increased only by the addition of organo-soluble (touluene soluble) surfactants (e.g. dodecyl benzene sulfonic acid). The presence of surfactants, however, can cause both printing and fastness problems, and furthermore the use of surfactants limits the quantity of dye that can be used in the printing inks. The present invention does not require the use of such surfactive materials.

While the use of the carbinols (dye precursors) of the above-mentioned colour families was not fully convincing, it has now been found that by using a particular group of basic (yellow) indole dyes and their carbinol precursors for preparing gravure printing ink compositions, outstanding effects can be achieved.

Accordingly, it is the main object of the present invention to provide said gravure printing ink compositions. Other objects of the present invention relate to processes for the preparation of these gravure prining ink compositions as well as methods of using them.
These and other objects of the present invention will be described in the following.

Therefore, in a first aspect, there is provided an organic solvent-based gravure printing ink composition which comprises
(1) a cationic dyestuff of formula (1),



(1)

or a mixture thereof,

wherein R_1-R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to form a homocyclic or heterocyclic aromatic or non-aromatic ring, m is an integer of 1 to 5, n is an integer of 1 to 4 and X^- is an organic anion,

(2) a non-polar organic solvent,

(3) optionally an organic acid, preferably a resin acid, or a salt thereof, soluble in the non-polar solvent, and

(4) optionally a pigment.

The substituents R_1-R_6 in formula (1) are independently of one another hydrogen; further substituted or unsubstituted alkyl and alkoxy which comprises species of e.g. 1 to 20 carbon atoms, preferably of 1 to 10 carbon atoms, which may be linear or branched. Examples are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, hexadecyl, octadecyl and the corresponding isomers. The alkoxy species can be listed analogously. Preferred are the lower alkyl/alkoxy (C_1-C_4) species, and mostly preferred are methyl and methoxy.

As to the substituted alky and alkoxy radicals (preferences with regard to the chain lengths as mentioned above) there can be mentioned hydroxyalkyls, halogeno-alkyls (fluoro-, chloro-, bromo-, iodo), aminoalkyls, cyanoalkyls and arylalkyls, wherein the aryl moiety may be further substituted (e.g. lower alkyl and alkoxy, halogeno, hydroxy, cyano, amino, carboxy, carbonamido), on the one hand, and e.g. arylalkoxy (aryl substituted as mentioned above), on the other hand.

The cycloalkyl radicals may contain 5 to 10 ring carbon atoms, preferred are the C_5-C_7 species, viz. cyclopentyl, cyclohexyl, and cycoheptyl, cycohexyl being mostly preferred. Possible substituents may be lower alkyl radicals, preferably methy and ethyl.
The aryl radicals may contain e.g. 6 to 10 cabon atoms, preferably comprising phenyl or naphthyl, optionally substituted by hydroxy, halogeno (fluoro-, chloro-, bromo-, iodo), amino, cyano, carboxy, carbonamido, or sulfo and sulfonamido.
The heteroaryl radicals preferably contain 5 to 10 ring atoms, comprising one or more, e.g. 1 to 3, nitrogen, oxygen or sulfur atoms. Examples may be imidazolyl, oxazolyl, thiazolyl, thienyl, pyrrolyl, pyrazolyl, triazolyl, pyridinyl, pyridazinyl, pyrimidyl, triazinyl, benzimidazolyl, benzoxazolyl and quinoxalinyl, including isomeric forms. With regard to the monocyclic radicals, those of 5 or 6 ring atoms are preferred.
Substituents may be selected from e.g. hydroxyl, halogen, amino and substituted amino, cyano, carboxyl (including esters and amides), sulfo, sulfoamide, lower alkyl.

The allyl radical may be optionally substituted by lower alkyl, halogen or cyano.

R_2 and R_3 may be combined together to form a 5 to 7-membered homocyclic or heterocyclic ring, such as cyclopentane, cyclohexane or tetrahydrofurane.

Further, the subtituents R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl (RCO-), alkylthio, arylthio, acylamino including carboxylamino (carbonamido) R-CO-NH- (R is.g. hydrogen, alkyl or phenyl) and sulfonylamino (sulfamido) R_1-SO_2-NH- (R_1 is e.g. alkyl or phenyl), alkylsulfonyl, arylsulfonyl or thiocyano, wherein the number of carbon atoms may be up to 10; depending on the the radicals the lower limit may be 1 (alkyl) or 6 (aryl).

Any two of R_5 or any two of R_6 my be combined together to form with the rings to which they are attached, annellated ring systems such as homocyclic or heterocyclic aromatic or non-aromatic mono- or bicyclic rings. The annellated rings may contain 6 to 10 ring atoms, and preferably are 5- or 6-membered saturated or unsaturated homocyclic rings (phenylene, cyclopentylene, cyclohexylene); or they contain as heterocyclic rings nitrogen, oxygen and/or sulfur atoms; examples are thienyl, furfuryl, pyrimidyl, pyridinyl, or the group –O-CH_2-O-CH_2-.

The index m is an integer of 1 to 5, preferably 1 to 3 or 1 or 2; the index n is an integer of 1 to 4, preferably 2, and mostly preferred 1.

The anion X^- is generally derived from organic acids, such as fatty acids of 8 to 24, preferably 8 to 18, carbon atoms which are linear of branched, saturated or unsaturated and include caprylic acid (C_8), pelargonic acid (C_9), capric acid (C_{10}), lauric acid (C_{12}), myristic acid (C_{14}), palmitic acid (C_{16}), stearic acid (C_{18}), mono-unsaturated oleic acid (C_{18}), di-unsaturated linoleic acid (C_{18}), tri-unsaturated linolenic acid (C_{18}), and erucic acid (C_{22}). The mentioned fatty acids may be unsubstituted or, furthermore, substituted, for example by hydroxy or chlorine, preferably hydroxy. Preferably, the mentioned carboxylic acids are unsubstituted.
Preferably, the fatty acids are saturated or mono-unsaturated C_{12}-C_{18}fatty acids.

Further acids may be 2-(2,4- ditert.-amylphenoxy)-butyric acid; phosphoric/phosphonic acids, such as the monolauryl ester of of phosphoric acid, the dioctyl ester of phosphoric acid or dodecyphosphonic acid; sulfonic acids, such as hexadecane sulfonic acid, alkyl substituted benzene sulfonic acids, such as p-toluene sulfonic acid or p-octylbenzene-sulfonic acid; naphthalene sulfonic acid or alkyl substituted naphthalene sulfonic acids; further phenolic acids, such as 3,5-di-tert.butylsalicylic acid; others are carboxylic acids having an unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl skeleton, for example 4-cyclohexylbutyric acid, 3-cyclohexylpropionic acid, cyclohexylacetic acid, cyclo-hexanecarboxylic acid, 4-methylcyclohexanecarboxylic acid and cyclopentanecarboxylic acid.

Preferably the anion X^- is derived from resin acids, i.e., carboxylic acids based on terpenes, for example acyclic, monocyclic or bicyclic C_{10}terpenes, acyclic, monocyclic, bicyclic or tricyclic C_{15}sesquiterpenes, acyclic, monocyclic or tricyclic C_{20}diterpenes, especially tricyclic C_{20}diterpenes, e.g. abietic acid, dihydroabietic acid and tetrahydroabietic acid. Preferred resin acids are colophony (main component abietic acid), rosin acid and abietyl resin as well as derivatives thereof.
The rosin acids include e.g. gum rosin, wood rosin and talloil rosin. Rosin derivatives may include disproportionated, hydrogenated, dimerised, polymerised or part-polymerised rosins; and further rosin modified esters, such as maleinized rosin, pentaerythritol rosin ester and rosin-modified phenolic resin.

The chromophores of the cationic (basic) dyes of formula (1) are e.g. compiled as C.I. Basic Dyes in The Colour Index (C.I.), issued by the Society of Dyers and Colorists and The American Association of Tectile Chemists and Colorists. Details of the dyes are disclosed there.

Component (2) of the inventive gravure printing ink compositions is a non-polar organic solvent which may be selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons (halogenated), preferably of the benzene series, glycol ethers, non-polar alcohols, esters, ketones, halogenated aliphatic hydrocarbons and mixtures thereof.

The aliphatic hydrocarbons are preferably those having a boiling point of about 75 to 180°C.

Typical examples are heptane, octane, nonane, decane and like normal paraffins, isootane and like iso-paraffins; ligroin, petroleum spirit, and refined gasoline, 1-heptene, 1-octene, 1-nonene.
The preferred aromatic hydrocarbons are those of the benzene series, particularly unsubstituted or C_1-C_4-alkyl substituted benzenes, such as benzene, xylene, and preferably toluene; and further halogenated benzenes, such as the the chlorobenzenes (mono-, di- and tri-).
As glycolethers there can be used e.g. ethylene glycol monomethyl and monoethylether, dipropylene glycol, ethyldiglycol, butyldiglycol or phenylglycol.
Non polar alcohols are e.g. C_4-C_8 alcohols, such as n-butanol or n-hexanol as well as the corrosponding isomers and further cyclohexanol and benzyl alcohol.
Representative esters are the acetates, such as ethyl acetate, propyl acetate or butylacetate.
Suitable ketones are methylethyl ketone, methylisobutyl ketone, cyclohexanone and acetophenone.
Preferred species of the halogenated aliphatic hydrocarbons are dichloromethane, trichloromethane, tetrachloromethane, trichloroethane, tetrachloroethane, trichloroethylene, tetrachloroethylene.
The organic acids which constitute component (3) of the inventive gravure printing ink composition are those mentioned hereinbefore when defining their anions X^-. Mixtures of acids can also be used.

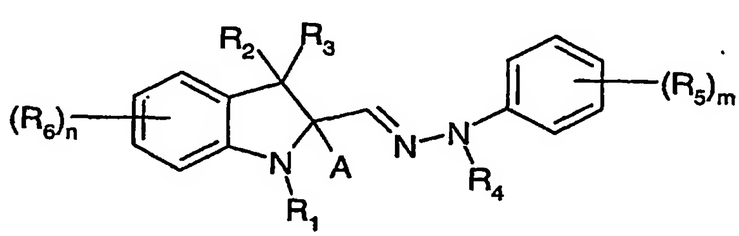
The acids used are as a rule not surfactive in nature and are perfectly compatible with the ink solvent and binders (ink vehicles).

Component (4) of the inventive compositions preferably relates to organic pigments which comprise, but not exclusively, such pigments as monoazo, disazo, naphthol, dioxazone, azomethin, azocondensation, metal-complex, nitro, perinone, quinoline, anthraquinone, benzimidazolone, isoindoline, isoindolinone, quinacridone, hydroxyanthraquinone, aminoanthraquinone, anthrapyrimidine, indanthrone, flavanthrone, pyranthrone, antanthrone, isoviolanthrone, diketopyrrolopyrrole, carbazole, perylene, indigo or thioindigo pigments. Mixtures of the pigments may also be used.
Preferred are organic pigments of the following chemical classes:
Monoazo, disazo, azomethin, naphthol, and metal-complex pigments (e.g. phthalocyanines).

For further details as to the organic pigments reference is made to *Industrial Organic Pigments*, W. Herbst, K. Hunger, 2nd edition, VCH Verlagsgesellschaft, Weinheim, 1997.

Optionally the organic pigments can be mixed with inorganic pigments which include among others titanium oxide pigments, iron oxide and hydroxide pigments, chromium oxide pigments, spinel type calcined pigments, lead chromate pigments, carbon black and Prussian Blue.
Alternatively, full replacement of organic pigments by inorganic ones is also possible.

The inventive gravure printing ink compositions can be prepared by a process which comprises mixing together
(a) a carbinol dye precursor of the formula (2)



(2)

or a mixture thereof, dissolved or dispersed in a non-polar organic solvent,
wherein R_1-R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl,

alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to a homocyclic or heterocyclic aromatic or non-aromatic ring, A is –OR, $-N(R)_2$, -N(R)COR, $-N(R)SO_2R$, -SR, -S(O)R, $-O_2CR$, $-N(R)CON(R)_2$, $-OCON(R)_2$, $-SO_2N(R)_2$ or –N(R)COOR, wherein R is R_1, m is an integer of 1 to 5 and n is an integer of 1 to 4, with

(b) a solution of an organic acid, preferably a resin acid, dissolved in a non-polar organic solvent, and with

(c) optionally a pigment.

Preferably, R_1-R_6 in the carbinol dye precursor of formula (2) are independently of one another hydrogen, unsubstitued or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and A, m and n have the meanings indicated. Mostly preferrred as substituent A is –OH.
As to further preferences of the substituents, reference is made to those definitions provided for them in formula (1).

As an alternative to this process, the preparation can be performed as follows:

This process comprises mixing together
(a) a carbinol dye precursor of the formula (2) with
(b) a solution of an organic acid, preferably a resin acid, dissolved in a polar or non-polar organic solvent,
evaporating off the solvent (under reduced pressure) from that mixture until a dry mixture is obtained, and redissolving the dry mixture in a non-polar solvent, and with
(c) optionally an (organic) pigment.

The polar organic solvents includes for example a C_1-C_4 aliphatic alcohol, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol or isobutanol; an amide, e.g. dimethylformamide or dimethyl acetamide; a ketone or ketone alcohol, e.g.

acetone, methyl isobutyl ketone, diacetone alcohol; an ether, e.g. tetrahydrofuran or dioxan; a nitrogen-containing heterocyclic compound, e.g. N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone; a polyalkylene glycol, preferably a low molecular weight polyethylene glycol having a molecular weight of from 100 to 800, e.g. diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol 200, polyethylene glycol 300, polyethylene glycol 400 or polyethylene glycol 600, especially having a molecular weight of from 150 to 400, or a low molecular weight polypropylene glycol, e.g. dipropylene glycol, tripropylene glycol, polypropylene glycol P 400 or polypropylene glycol P 425; a C_1-C_4alkyl ether of a polyalkylene glycol, e.g. diethylene glycol monobutyl ether, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol or 2-[2-(2-ethoxyethoxy)ethoxy]ethanol; a C_2-C_6alkylene glycol or a thioglycol, e.g. ethylene glycol, propylene glycol, butylene glycol, 1,5-pentanediol, thiodiglycol, hexylene glycol; further a polyhydric alcohol, e.g. glycerol or 1,2,6-hexanetriol; or a C_1-C_4alkyl ether of a polyhydric alcohol, e.g. 2-methoxyethanol or 1-methoxypropan-2-ol.

Further, the inventive process additionally comprises mixing a so-called ink vehicle with the combined dry, or wet, or redissolved components (a), (b) and optionally (c).
These ink vehicles which are in general any known oily binders include for example long-oil-, medium-oil- or short oil-alkyd resins, phenol-modified alkyd resins, phenolic resins, rosin-modified phenolic resins, metal resinates, such as copper, zinc or magnesium resinate, petroleum resins, (cyclic) hydrocarbon resins, such as terpene or terpene-phenolic resins, resins based on acrylics, styrenes and vinyl polymers, melamine and epoxy resins, distillate and vegetable oils.

Alternatively, the inventive process may be carried out by dry mixing components (a), (b) and optionally (c), and then co-dissolving this mixture in a non-polar organic solvent as hereinbefore defined.
The wet blend (co-dissolved mixture – as solution or in concentrated form) is a further object of the present invention.
The dry mixture of components (a), (b) and optionally (c) used according to this alternative is a further object of the present invention.

Alternatively, the inventive process compomprises dry mixing components (a), (b) and optionally (c), and an ink vehicle, and then co-dissolving this mixture in a non-polar solvent.

The dry mixture of components (a), (b) and optionally (c), and an ink vehicle used according to this alternative is a further object of the present invention.
The wet blend (co-dissolved mixture – as solution or in concentrated form) is a further object of the present invention.

As a further alternative, the inventive process comprises incorporating components (a), (b) and optionally (c) separately or as dry mix into preformed ink vehicles.
This process can be carried out by extruding the components (a), (b) and optionally (c) separately or as dry mix into high solids dispersions, solutions or pastes of the ink vehicle.
The extrusion products obtained according to this process are a further object of the present invention.
The organic/inorganic pigments (c) are those as defined hereinbefore as component (4).

Mostly preferred are compounds of formula (2) to be used in the inventive process, wherein R_1-R_4 are methyl, R_5 is methyl or methoxy (m is 1), two R_5 together form $-O-CH_2-O-CH_2-$, R_6 is hydrogen, A is -OH and n is 1.

Further, the inventive process is carried out, wherein components (b) and (c) together constitute a resinated pigment.

The essential components and the optional components can be mixed by any known method using a ball mill, sand mill, bead mill, attritor, continuous horizontal medium dispersing machine, two-roll mill, three-roll mill, pressure kneader, or extruder; further by manual or mechanical shaking, or by low or high shear stirring.

The conventional process for preparing a pigment based gravure ink composition may be carried out in two steps:
(I) The dissolving of the ink vehicle in the non-polar organic solvent (toluene).
(II) The dispersion of the pigment within the dissolved ink vehicle.
Step (II) normally requires a far higher level of shear than step (I) and results in the generation of heat.
It has now been found that preparing the inks according to the present invention is extremely flexible which can be shown by the following manufacturing methods all of which produce identical inks:

- The organic acid (resin acid) is fully dissolved in the non-polar organic solvent (toluene) followed by the carbinol. The dye solution thus produced is added to a previously prepared ink vehicle solution.
- The organic acid (resin acid) and carbinol are dry mixed together and then codissolved in the non-polar organic solvent (toluene). The dye solution thus produced is added to a previously prepared ink vehicle/toluene solution.
- The organic acid (resin acid), carbinol and ink vehicle resin are dry mixed together and then co-dissolved in the non-polar organic solvent (toluene).

In all three cases the level of shear require is similar to that necessary for normal dissolving of ink vehicle resins and far less than that required for pigment dispersion. Due to the lower shear, the generation of heat within the inks is much reduced.
It is therefore possible to produce a finished coloured ink within the same timescale and using similar shear to that normally required for the simple dissolving of the ink vehicle resin.

Due to the simplicity of reaction, many processing possibilities are now open. The production of a coloured ink can now be carried out on any equipment capable of generating low levels of shear. The traditional high shear approach to pigment dispersion is not required though the possibility of carrying out both in tandem is included.

Combination of the carbinol with the resin acid can be carried out in an extruder with a suitable carrier system. This carrier system may be a solvent or a concentrate of a suitable ink vehicle. Reaction of the carbinol may be achieved during the extrusion process though this is not essential as this can occur during the later dispersion of the concentrate within the ink solvent.

The carbinol approach to colouration can be used in conjunction with traditional pigment methodology. As such, further possibilities for both ink and pigment processing are opened.

In general, conventional publication gravure pigments do not contain high levels of abietyl resins (resin acid) as part of their compositions. Such resins are commonly used in pigments destined for use in distillate or vegetable oil based offset lithographic inks. In addition to improving the performance of the pigment within the ink system further advantages are also gained. The abietyl resin treatments act to reduce aggregation of the pigment during

production and drying. Abietyl resin containing pigments in general can be produced more quickly and more reproducibly while also giving products of much reduced aggregation. As a result the dispersibility of the product and the final performance are often superior.

Conventionally, toluene based publication gravure inks have not utilised abietyl resin containing pigments as the solution of this material into the ink vehicle causes increased viscosity. However, as abietyl resins are acidic in nature, the possibility now exists to use this material as a converting agent for carbinol dye pre-cursors. Thus the pigment can be considered as a carrier for the carbinol-converting agent. The carbinol can also be considered as an agent that reduces the traditional problems of using resinated pigments in toluene systems. The high colour strength of the resulting dyestuff allows the use of a lower pigmentation level thus reducing viscosity. The possibility also exists for improved gloss thus allowing an equivalent reduction in binder level.

The inventive compositions may be employed in any amount effective for the intended purpose. In general good results have been obtained with compositions which comprises by weight 0.1-50 % of component (1), 5 - 95% % of component (2), 0 - 50 % of component (3), and 0 – 50 % of component (4).
Preferably the concentrations may be: 15-40 % of component (1), 40-60 % of component (2), 20-50 % of component (3), and 0-50 % of component (4).

The compositions may be generally embodied in the following two forms:
(A) A composition containing components (1) to (3) but no pigment – this composition can be used itself as gravure printing ink (whole colourant composition).
(B) A composition containing components (1) to (4) wherein components (1) to (3) serve as toning agents for the shading, tinting and brightening of predominatly pigment (4) based inks (partial colourant composition).

The acid, preferably the resin acid, of component (3) is the excess acidic component from the reaction with the carbinol precursor. Though most experimental work has required high levels of the acidic component to push the reaction forward. It is possible that a 1:1 molar reaction with the carbinol can be done.
Thus the excess (component (3)) may have to start from 0 %. It is also used possible that the excess acidic component is used to make up the majority of the gravure binder resin

composition (gravure binder resins are often derivatives of resin acids such as metal resinate salts) and therefore can become an amount of up to 50%.
The amount of component (3) is therefore defined as of 0 to 50%.

Furthermore, the printing inks may in addition comprise customary additives known to those skilled in the art.
Typical additives include drying enhancers, drying inhibitors, non-coloured extenders, fillers, opacifiers, antioxidants, waxes, oils, surfactants, rheology modifiers, wetting agents, dispersion stabilizers, strike-through inhibitors and anti-foaming agents.
Such additives are usually used in amounts of from 0 to 2% by weight, preferably from 0.01 to 1% by weight, based on the totaol weight of the gravure printing ink composition.

The inventive gravure printing ink compositions can be used in the corresponding processes for gravure printing of (flat) substrates, such as publication gravure printing and packaging gravure printing. These processes are further objects of the present invention.

While publication gravure printing is used for magazines, magazine supplements, mail-order catalogs, and other areas, packaging gravure printing is used for packaging materials, such as paper or plastic films.

The present invention is hereafter further described with reference to particular examples thereof. It will be appreciated that these examples are presented for illustrative purposes and should not be constructed as a limitation on the scope of the invention as herein described.

In the following examples, quantities are expressed as parts by weight or percent by weight, if not otherwise indicated.
The temperatures are indicated in degrees centigrade.

Examples

Example 1

11.2g of tall oil rosin is added to 14.3g toluene and shaken until dissolved. To this solution, 4.5g of the carbinol base of C.I. Basic Yellow 29 is added and shaken until full solution is achieved. 20.0g of this dyestuff solution is then combined with 80g of a 50% toluene solution of rosin modified phenolic resin.

Example 2

9.0g of tall oil rosin is added to 15.0g toluene and shaken until dissolved. To this solution, 6.0g of the carbinol base of C.I. Basic Yellow 28 is added and shaken until full solution is achieved. 20.0g of this dyestuff solution is then combined with 80g of a 50% toluene solution of rosin modified phenolic resin.

Comparative Example A

A traditional pigment based publication gravure ink is prepared by beadmilling 7.0g IRGALITE Yellow PR26® (C.I. Pigment Yellow 12 composition) into 70.0g of a 50% rosin modified phenolic resin solution in toluene and a further 23.0g toluene.

Comparative Example B

A traditional pigment based publication gravure ink is prepared by beadmilling 7.0g PERMANENT Yellow DHG N20® (C.I. Pigment Yellow 12 composition) into 70.0g of a 50% rosin modified phenolic resin solution in toluene and a further 23.0g toluene. The prints of Comparative Example B are moderately more red shade than Comparative Example A.

Strength gloss and transparency versus pigment

	Comparative Example A	Example 1
COLOURANT CONTENT (BY WEIGHT)	7.0%	3.0%
STRENGTH	100%	100-105%
GLOSS	standard	slightly-moderately higher
TRANSPARENCY	standard	moderately-considerably higher

Shade match by ink blending

	Comparative Example B	80/20 BLEND OF EXAMPLE 1/EXAMPLE 2
COLOURANT CONTENT (BY WEIGHT)	7.0%	2.4% and 0.8% respectively
STRENGTH	100%	105% and very slightly cleaner
GLOSS	standard	moderately higher
TRANSPARENCY	standard	moderately higher

Colour enhancement of gravure pigment

	COMPARATIVE EXAMPLE A	75/25 BLEND OF EXAMPLE 1 AND COMPARATIVE EXAMPLE A
COLOURANT CONTENT (BY WEIGHT)	7.0%	5.2% and 1.0% respectively
STRENGTH	100%	125%
GLOSS	standard	as standard
TRANSPARENCY	standard	slightly-moderately higher

Fastness versus pigment

PRINT FASTNESS PROPERTY	COMPARATIVE EXAMPLE A	EXAMPLE 1
LIGHT (BLUE WOOL SCALE – 72 HOURS)	3	3
SWEAT	5	5
SALIVA	5	5

Rheology

Example 3

The methodology of Example 1 is repeated replacing the 80.0g of 50% toluene/phenolic medium with 70.0g and 10.0g toluene.

FLOW MEASUREMENT	COMPARATIVE EXAMPLE A	EXAMPLE 1	EXAMPLE 3
ZAHN CUP No. 2	51	65	26
ZAHN CUP No. 3	17	19	9
Note that the gloss, strength and transparency of Example 3 were identical to Example 1.			

Dye solution manufacture using alternative rosins:

Example 4

11.2g tall oil rosin is dissolved in 17.3g toluene by shaking. 4.5g of the carbinol base of Basic Yellow 29 is then added and shaking continued until full solution is achieved.

Example 5

Example 4 is repeated where tall oil rosin is replaced by disproportionated rosin.

Example 6

Example 4 is repeated where tall oil rosin is replaced by hydrogenated rosin.

Example 7

Example 4 is repeated where tall oil rosin is replaced by gum rosin.

Example 8

Example 4 is repeated where tall oil rosin is replaced by maleic modified rosin.

Example 9

Example 4 is repeated where tall oil rosin is replaced by oleic acid.

Example 10

Example 4 is repeated where tall oil rosin is replaced by dodecylbenzenesulphonic acid.

Comparison of Examples 4-10

Examples 4 to 10 all give full coloured solutions indicating effective conversion of the carbinol and compatability with toluene. Even without the addition of an ink vehicle, the film-forming properties and gloss of Examples 4 to 8 is such that printing can be achieved. Only very mild shade differences are seen between these examples. Much reduced gloss is obtained with Examples 9 and 10. The prints from 9 and 10 remain tacky for a longer period of time and the resistance to moisture is also greatly reduced in comparison with Examples 4 to 8.

Other rosin acids give useable dyestuff solutions:

Example 11

Example 4 is repeated where tall oil rosin is replaced by dimerised rosin.

Example 12

Example 4 is repeated where tall oil rosin is replaced by polymerised rosin.

Processing advantage:

Example 13

In a screw-cap jar, 11.2g tall oil rosin is dissolved in 14.3g toluene by shaking. 4.5g Basic Yellow 29 carbinol base is added and dissolved by shaking. 20g of this solution is then taken and added to 80g of a 50% solution of rosin modified phenolic resin in toluene.

Example 14

In a screw-cap jar, 11.2g tall oil rosin is dry mixed with 4.5g C.I. Basic Yellow 29 carbinol base and 14.3g toluene then added. Full solution is achieved by shaking. 20g of this solution is then taken and added to 80g of a 50% solution of rosin modified phenolic resin in toluene.

Comparative Example C

In a screw-cap jar, 50g rosin modified phenolic resin is added to 50g of toluene. 7 sessions of 4 minutes are required on a mechanical shaker at 1000rpm to achieve full solution.

Example 15

In a screw-cap jar 7.5g tall oil rosin, 3g C.I. Basic Yellow 29 carbinol base and 40g of rosin modified phenolic resin are dry mixed then 49.5g toluene is added. 7 sessions of 4 minutes are required on a mechanical shaker at 1000rpm to achieve full solution.

Note that the inks produced in Examples 13, 14 and 15 display identical properties. The final compositions of the three final inks are identical. Note also that the ink in Example 15 can be produced with the same level of energy input as the resin solution in Comparative Example C.

Comparative processing examples with pigment:

Comparative Example D

In a screw-cap jar 7.5g tall oil rosin, 3g Irgalite Yellow PD 4071 (Ciba Pigment Yellow 12 composition tailored for publication gravure, similar to the aforementioned PR26) and 40g rosin modified phenolic resin are dry blended then 49.5g toluene added. The mixture is then subjected to the same shaking process as used in Example 15.

Comparative Example E

Comparative Example D is repeated with the inclusion of 200g 1.7-2mm glass beads to give a far higher level of shear.

Comparative Example F

Comparative Example E is repeated with the tall oil rosin omitted and replaced by a further 7.5g rosin modified phenolic resin. This sample replicates the total solids and colourant level in Example 15 though is carried out with higher shear.

Comparative Example G

Comparative Example E is repeated with the pigment charge increased to 7.5g in an attempt to match the colour strength possible from the Example 15 ink.

Results of Example 15 against comparative examples D to G

Comparative Example D shows poor dispersion of the colourant with severe settled solids in the vessel.

Comparative Example F contains lumps of undispersed resinous material.

Comparative Example G has congealed and is far too thick for manipulation by normal toluene-based ink techniques. Incomplete resin dispersion is also noted which does not improve on a further 3 sessions of 4 minutes on the mechanical shaker.

Comparative examples E, F and G are extremely hot (cannot be held comfortably in the hand) while Example 15 and Comparative Example D are only mildly warm to the touch.

Dispersion level by microscope (x100 magnification) assessment.

Example 15 is a complete solution.

Comparative Example D contains large quantities of over-sized undispersed particles.

Comparative Examples E and F contain a significant quantity of finer undispersed particles.

Comparative Example G contains both the large quantity of over-size particles and the significant amount of undispersed finer material.

Hegman Gauge Readings (0-100 micron)

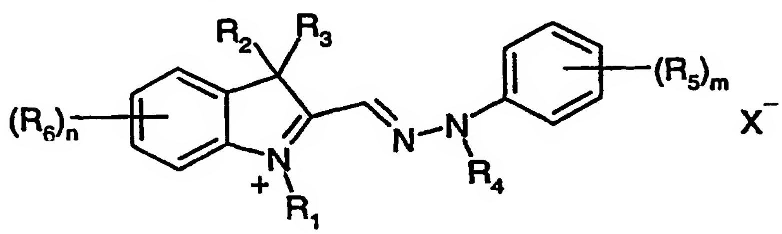
With this level of dispersion analysis, recordings are made of the points where 3 (three) different forms of disturbance to the ink film are first observed. Values between 0 and 8 are assigned where lower figures indicate earlier disturbance and larger particle size.

Example 15 –	8/8/6.5
Comparative Example D –	5/1/1
Comparative Example E –	8/6.5/3.5
Comparative Example F –	8/6.5/3.5
Comparative Example G –	8/7/4

Claims:

1. An organic solvent-based gravure printing ink composition which comprises

(1) a cationic dyestuff of formula (1),



(1)

or a mixture thereof,

wherein R_1-R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to form a homocyclic or heterocyclic aromatic or non-aromatic ring, m is an integer of 1 to 5, n is an integer of 1 to 4 and X^- is an organic anion,

(2) a non-polar organic solvent,

(3) optionally an organic acid, preferably a resin acid, or a salt thereof, soluble in the non-polar solvent, and

(4) optionally a pigment.

2. The composition according to claim 1, wherein R_1-R_6 in the dyestuffs of formula (1) are independently of one another hydrogen, unsubstitued or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and X^-, m and n have the meanings indicated.

3. A composition according to claim 2, wherein substituted alkyl comprises hydroxyalkyl, halogenoalkyl, aminoalkyl, cyanoalkyl or arylalkyl, substituted alkoxy comprises arylalkoxy, and aryl preferabvly comprises phenyl or naphthyl, optionally substituted by hyroxy-, halogeno-, amino-, cyano-, carboxy-, carbonamido-, sulfo- or sulfonamido.

4. The composition according to claim 2, wherein R_1-R_4 are methyl, R_5 is methyl or methoxy (m is 1), two R_5 together form –O-CH_2-O-CH_2-, R_6 is hydrogen and n is 1.

5. The composition according to any one of claims 1 to 4, wherein X^- is the anion of an organic acid, preferably a resin acid.

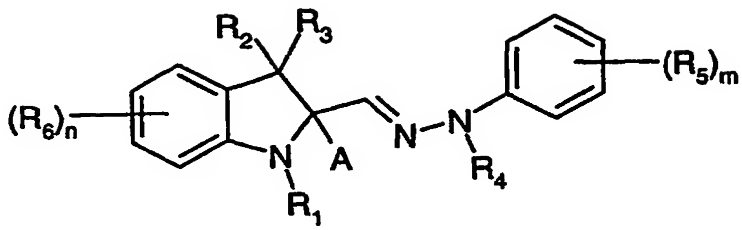
6. The composition according to claim 1, wherein the non-polar organic solvent (2) is selected from the group consisting of aliphatic hydrocarbons, optionally halogenated, or aromatic hydrocarbons, optionally halogenated, preferably of the benzene series, glycol ethers, non-polar alcohols, esters, ketones and mixtures thereof.

7. The composition according to claim 5, wherein the resin acid (3) is an organo-soluble acid selected from the group consisting of rosin acid, abietyl resin, colophony or derivatives thereof.

8. The composition according to claim 1, which comprises
0.1 - 50 % by weight of component (1),
5 - 95% % by weight of component (2),
0 - 50 % of component (3), and optionally
0 - 50 % of component (4).

9. The composition according to any one of claims 1 to 8 which additionally comprises an ink vehicle.

10. A process for the preparation of gravure printing ink compositions according to claim 1 which comprises mixing together
(a) a carbinol dye precursor of the formula (2)



(2)

or a mixture thereof, dissolved or dispersed in a non-polar organic solvent, wherein R_1-R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to a homocyclic or heterocyclic aromatic or non-aromatic ring, A is –OR, -N(R)$_2$, -N(R)COR, -N(R)SO$_2$R, -SR, -S(O)R, -O$_2$CR, -N(R)CON(R)$_2$, -OCON(R)$_2$, -SO$_2$N(R)$_2$ or –N(R)COOR, wherein R is R_1, m is an integer of 1 to 5 and n is an integer of 1 to 4, with

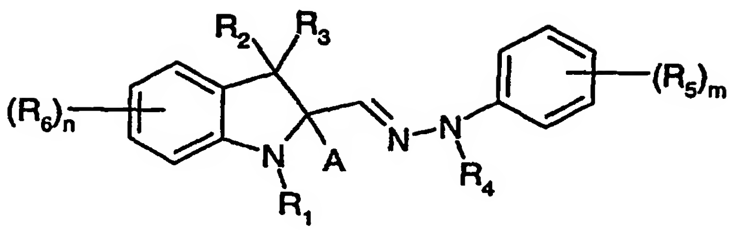
(b) a solution of an organic acid, preferably a resin acid, dissolved in a non-polar organic solvent, and with

(c) optionally a pigment.

11. The process according to claim 10, wherein R_1-R_6 in the carbinol dye precursor of formula (2) are independently of one another hydrogen, unsubstitued or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and A m and n have the meanings indicated.

12. A process for the preparation of gravure printing ink compositions according to claim 1 which comprises mixing together

(a) a carbinol dye precursor of the formula (2)



(2)

or a mixture thereof, dissolved or dispersed in a non-polar organic solvent, wherein R_1-R_6 are independently of one another hydrogen, substituted or unsubstituted alkyl, alkoxy, cycloalkyl, aryl, heteroaryl or allyl, R_2 and R_3 may be combined together to form a ring, further R_5 and R_6 are independently of one another halogen, cyano, nitro, aryloxy, alkenyl, alkenoxy, alkoxcarbonyl, aryloxycarbonyl, acyloxy, acyl, alkylthio, arylthio, acylamino, alkylsulfonyl, arylsulfonyl or thiocyano, any two of R_5 or any two of R_6 may be combined together to a homocyclic or heterocyclic aromatc or non-aromatic ring, A is –OR, -$N(R)_2$, -N(R)COR, -$N(R)SO_2R$, -SR, -S(O)R, -O_2CR, -N(R)CON$(R)_2$, -OCON$(R)_2$, -$SO_2N(R)_2$ or –N(R)COOR, wherein R is R_1, m is an integer of 1 to 5 and n is an integer of 1 to 4, with

(b) a solution of an organic acid, preferably a resin acid, dissolved in a polar or non-polar organic solvent,

evaporating off the solvent (under reduced pressure) from that mixture until a dry mixture is obtained, and redissolving the dry mixture in a non-polar solvent, and with

(c) optionally an organic pigment.

13. A process according to claim 12, wherein R_1-R_6 in the carbinol dye precursor of formula (2) are independently of one another hydrogen, unsubstitued or substituted alkyl or alkoxy of 1 to 10 carbon atoms, cycloalkyl of 5 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, heteroaryl of 5 to 10 atoms, comprising one or more nitrogen, oxygen or sulfur atoms as ring members, or allyl, R_2 and R_3 may be combined together to form a 5 to 7-membered ring, and A, m and n have the meanings indicated.

14. A process according to claim 13, wherein R_1-R_4 are methyl, R_5 is methyl or methoxy (m is 1), two R_5 together form –O-CH_2-O-CH_2-, R_6 is hydrogen, A is -OH and n is 1.

15. A process according to claim 10, wherein components (b) and (c) together constitute a resinated pigment.

16. A process according to any of claims 10 to 15, wherein the polar organic solvent for component (b) is a member selected from the group consisting of C_1-C_4 aliphatic alcohols, amides, ketones, ethers, N-heterocyclic compounds, C_2-C_6 alkylene glycols or thioglycols, polyalkylene glycols and their C_1-C_4 alkyl ethers, and polyhydric alcohols and their C_1-C_4 alkyl ethers.

17. A process according to claim 12, which additionally comprises mixing an ink vehicle with components (a), (b) and optionally (c).

18. A process according to claim 12, which additionally comprises mixing an ink vehicle with the combined dry or redissolved components (a) and (b), and optionally component (c).

19. A process for the preparation of gravure printing ink compositions according to claim 1, which comprises dry mixing components (a) and (b), and optionally with component (c), and then co-dissolving this mixture in a non-polar organic solvent.

20. The dry mixture of components (a) and (b), and optionally (c), used in the process according to claim 19.

21. The co-dissolved mixture of components (a), (b), and optionally (c) obtained according to claim 19.

22. A process according to claim 17, which comprises dry mixing components (a), (b) and optionally (c), and an ink vehicle, and then co-dissolving this mixture in a non-polar solvent.

23. The dry mixture of components (a), (b), optionally (c), and an ink vehicle used in the process according to claim 22.

24. The co-dissolved mixture of components (a), (b), optionally (c), and an ink vehicle obtained according to the process of claim 22.

25. The process according to claim 17, which comprises incorporating components (a), (b) and optionally (c) separately or as dry mix into preformed ink vehicles.

26. The process according to claim 22, which comprises extruding the components (a), (b) and optionally (c) separately or as dry mix into high solids dispersions, solutions or pastes of the ink vehicles.

27. The extrusion products obtained according to the process of claim 26.

28. Use of the composition according to any one of claims 1 to 9 as gravure printing inks.

29. Use of the composition according to any one of claims 1 to 9 as toning agents for predominantly pigment based gravure printing inks.

30. Process for gravure printing which comprises printing a flat substrate with a printing ink composition according to any one of claims 1 to 9.

31. Process for gravure printing which comprises printing a flat substrate with a predominantly pigment based printing ink containing a compositions according to any one of claims 1 to 9 as toning agents.

32. Process according to any one of claim 30 or 31 wherein the gravure printing process is a publication gravure or packaging gravure printing process.

Abstract:

An organic solvent-based gravure printing ink composition which comprises a cationic dyestuff of the indole class, a non-polar organic solvent, an organic acid which preferably is a resin acid, soluble in the non-poar solvent, and optionally an organic pigment.

The cationic dyestuff is formed (in situ) from its carbinol precursor. The compositions show for example high colour strength and excellent rheological properties and can be used in publication gravure or packaging gravure printing processes.